

SOIL SURFACE FLUX MEASUREMENT: USES AT LAWRENCE LIVERMORE NATIONAL LABORATORY (LLNL)

Stan Martins, LLNL

Introduction:

An emission isolation flux chamber is an enclosure of known volume. The chamber has an open end with a known area that is placed on the soil surface to quantify fugitive soil emissions. The chamber contains several penetrations that are used to introduce “sweep air”, to allow chamber-air to exit, and to deploy temperature and pressure sensors.

Soil surface flux (SSF) is the rate of exchange of one or more gases between soils and the atmosphere. An emission isolation flux chamber is used to measure this rate by placing the chamber on a soil surface and passing very pure sweep-air at a known rate through the chamber. Gases that diffuse from the soil surface enter the flux chamber and mix with the sweep air. Once the gases in the chamber are at equilibrium with gases emitted from the soil, the concentration of each target gas in the chamber is measured. If the target gas is a VOC, the flux rate is calculated as $\text{g/m}^2/\text{min}$ of this substance. If the target gas is tritium or radon, the flux rate is calculated as $\text{pCi/m}^2/\text{min}$.

Applications:

SSF measurements have been made at many different LLNL Main Site and Site 300 locations, as well other non-LLNL locations. We have measured the flux rates of VOCs, tritium, and noble gases. Flux measurements have been used to monitor the progress of remediation, to identify new areas of contamination, to monitor the progress of an infiltration study, to identify the source of soil contaminants, and to study barometric pumping.

The Sites

Building 518

Soils in the Building 518 area contain VOCs as a result of unplanned releases from an adjacent solvent storage yard. These releases resulted in high concentration VOCs in the vadose zone. SSF measurements were made monthly at five different sites between 9/92 and 7/93. Each site was located over zones of known VOC soil-vapor concentration (from about 20 ppmv to about 1800 ppmv) as determined by a soil vapor survey of gas samples taken at depths of five feet. The correlation between SSF measurements of VOCs and the results of the soil vapor survey were good, with an average $R^2 = 0.984319$ (Std = 0.0148) between 10/92 and 5/93.

In June of 1993, a vapor extraction feasibility test was performed over a period of three days (Berg et al., 1994). During this test, soil gas was extracted from the site where the VOC concentration was highest. Extractions were performed with vacuums as high as 18" Hg and flow rates as high as 100 standard cubic feet per minute (SCFM) for periods up to 10 hours each day. Surface flux measurements made during this time showed that VOC emissions from the soil surface dropped over the course of each day. The SSF rates partially recovered over night when the pumping ceased. SSF measurements made at all five sites during this test demonstrated a reduced correlation (when compared to earlier results) between SSF results and soil vapor survey results, with $R^2 = 0.638229$.

By July 20, 1993 the correlation between the soil vapor survey results and SSF measurements was $R^2 = 0.945688$. Because the correlation between soil vapor survey results and SSF did not return to their former levels, it is likely that the three days of vapor extraction during the test permanently changed the VOC concentration in the vadose zone around the extraction borehole. Subsequent calculations made with the analytical data from this test indicate that about 10 Kg of VOCs were removed from the soil.

In October of 1995, a vapor extraction treatment facility went on line at this site, with an extraction rate of about 15 SCFM and a vacuum of 5" Hg. By July of 1996 an additional 51 Kg of VOCs had been removed from these soils. At the end of this time, SSF emissions had been reduced by 95% over soils with the highest initial vapor concentrations and were undetectable over soil with the lowest concentrations.

Seasonal variations in SSF rates were noted during these studies, with the highest rates observed in September and the lowest rates observed in January or February. This seems to be correlated with the amount of water saturation of the soil. Our rainy season is usually between October and April, with little or no rain between June and September.

Health Risk Assessment

Because high concentrations of VOCs are found in soils at four different locations at LLNL Site 300 and at one site at the Stanford Linear Accelerator in Palo Alto, it was determined that health risk assessments should be made at each of these sites. SSF measurements made at each site were used with a box model to develop these health risk assessments. The results of using this model with SSF generated data indicated that no active remediation was required at any of these sites. One might conclude that remediation was required if only VOC analytical data from soil cores were used to model the health effects of soil off gassing. The reason for this discrepancy is that no matter how many soil cores are sampled, these data can never be very representative of the whole area. SSF results actually represent the amount of off-gassing at the surface, and does not depend on a model to arrive at these estimates (Carlsen et al., 1996; Carlsen et al., 1995).

Hanford Passive Remediation Investigation

A large plume of Carbon Tetrachloride (CCl_4) resulted from releases in soils under a Hanford, WA plutonium facility many years ago. CCl_4 soil vapor concentrations at the periphery of this plume are high enough to be of concern, but too low to make active remediation economical. As part of a feasibility study to determine the efficacy of passive remediation, two flux chambers were set up over this plume, and continuous SSF measurements were made for a period of three days. Analysis of these data shows that diurnal changes in the SSF rate of CCl_4 were proportional to changes in barometric pressure. As a result of these and other measurements, attempts to install a pilot-scale passive remediation system were made.

Vadose Zone Observatory: The vadose zone observatory was constructed in 1997 over uncontaminated soils and was designed to study the fate of substances injected into soils as gas or with water. As part of these studies, a cocktail of several noble gases was injected into a well that was screened at 15 to 16 feet. SSF measurements were made three different times after the initial injection from 0 to 30 feet away from the injection point. Analysis of the SSF samples by mass spectrometer revealed that portions of the noble gas cocktail were escaping from the soil at distances as great as 20 feet (Ralson et al., 1999; Carrigan et al., 1999; Carrigan et al., 1998).

Building 511

Recently, VOCs have been detected in ground water under the Building 511 area. A general survey of this area with SSF measurements has identified a possible source of this plume. Plans have been made to make a more detailed survey of the area, so that remediation by soil-vapor extraction may start when an extraction skid is available.

Building 292

The vadose zone under the Building 292 area at LLNL was contaminated by tritium from a leaking underground tank some time between 1986 and 1989. Soil over the release site has been covered with asphalt, but there is bare soil within 10 feet of the tank.

Several SSF measurements were made at this site, some over bare soil and others over asphalt. Because tritium at this site is in the form THO, most of the tritium is found in soil gas as water vapor. The sweep air for these measurements was circulated through the chamber by a pump. Air pumped from the chamber was passed through a cold trap where most of the water vapor was condensed and frozen as water ice. This air was then re-introduced into the chamber. After the chamber was purged for 35 minutes through a cold trap, the air stream was switched to a new cold trap where the SSF sample was collected. At the end of the sampling period, the sample was thawed, its volume measured, and tritium content measured by scintillation counter. The flux rate was then calculated as $\text{pCi/m}^2/\text{min}$.

The results of this study were interesting because water condensed from three SSF vapor samples taken between 12/92 and 3/93 contained less tritium than water condensed from

vapor in ambient air during each SSF sample period. This suggests that the atmospheric release of tritium from some other source was greater than that released from the soil above the tank leak.

Advances in Mass Spectrometry make this analytical technique an attractive alternative to the use of a scintillation counter to detect tritium. The major advantages of using the newer technique are that sample time could be reduced to minutes from hours and that detection limits could be improved.

Building 5475

Soils under the Building 5475 area contain both tritium and VOCs. VOCs were introduced into these soils during the Second World War as a result of aircraft engine maintenance in the area. Later on, tritiated-water evaporation ponds were constructed in the area. These ponds eventually formed leaks and tritium escaped into these soils by infiltration.

SSF measurement at six different sites revealed the presence of PCE in concentrations of 0.02 to 0.4 $\mu\text{g}/\text{m}^2/\text{min}$. on at least one occasion, while TCE was present at only one of these sites.

The tritium concentration in these samples was so low that no tritium was detected in SSF samples taken in this area. Use of a Mass Spectrometer instead of scintillation counting may have dropped the detection limit to the point where a flux rate could have been made (Berg et al., 1998).

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